

[DOCUMENT NAME] SPECIFICATION

[TITLE OF THE INVENTION] NONAQUEOUS ELECTROLYTE BATTERY

[TECHNICAL FIELD]

The present invention relates to nonaqueous
5 electrolytic lithium secondary batteries.

[patent literature 1] Japanese patent No. 2981545

[patent literature 2] JP 2003-373704 A

[patent literature 3] JP 2003-203674 A

[patent literature 4] JP 2003-288939 A

10 [nonpatent literature 1] Ionics, 3,356 (1997)

[nonpatent literature 2] Electroanalytical Chemistry and
Interfacial Electrochem., 53, 329-333 (1974)

[BACKGROUND ART]

Lithium ion secondary cells have been improved in
15 performance in recent years for use as power sources for
mobile devices. Lithium secondary cells are expected to be
useful in the field of peak-shift power sources and motor
vehicle assisting power sources from the viewpoint of the
energy density of the secondary cell, and it is desired that
20 these cells be further improved in service life and
reliability. Lithium secondary cells presently available
generally comprise a ceramic oxide serving as a positive
electrode active substance for lithium ions to be inserted
thereinto and released therefrom, metallic lithium or a
25 lithium alloy, or a carbon material or silicon material for
absorbing and desorbing lithium ions for use as a negative
electrode, and an electrolytic solution containing a lithium
salt as dissolved in an organic solvent.

However, organic solvents used in the above electrolytic solution are usually volatile and inflammable, hence have problem in safety. Contrary to organic solvent, salts melting at room temperature have characteristics of being nonvolatile and flame-retardant and have been expected to be applicable to electrolytic solutions for lithium secondary cells.

Typical examples of salts melting at room temperature include 1-ethyl-3-methylimidazolium tetrafluoroborate (EMI • BF₄). However, the imidazolium salt decomposes at a nobler potential than lithium and is therefore difficult to apply to lithium secondary cells. Studies are under way in recent years on salts melting at room temperature and remaining stable over a wider range of potentials.

For example, Nonpatent Literature 1 has revealed that salts comprising bis(trifluoromethanesulfonyl)imide anion and an aliphatic ammonium cation include compounds having a melting point not higher than room temperature and exhibiting improved electrochemical stability.

Patent Literature 1 shows that aliphatic quaternary ammonium salts melting at room temperature are applicable to lithium secondary cells. However, Patent Literature 1 merely discloses that lithium will deposit and dissolve on a nickel substrate in the aliphatic room temperature molten salt.

Nonpatent Literature 2 reveals that when graphite which is in wide use as the negative electrode material for lithium secondary cells is used as an electrode in a bath containing ammonium cations, the ammonium cations are decomposed or

inserted in between graphite layers. In connection with these problems, Patent Literature 2 discloses a nonaqueous electrolytic secondary cell which is characterized by having a room temperature molten salt and having vinylene carbonate or like cyclic ester, and shows that the presence of the cyclic ester forms on the surface of the negative electrode material a protective film for inhibiting reductive decomposition of cations of the room temperature molten salt, consequently giving stabilized charge-discharge characteristics.

Patent Literature 3 and Patent Literature 4 disclose a nonaqueous electrolytic cell containing an aliphatic room temperature molten salt, and a nonaqueous electrolytic lithium secondary cell having high safety and satisfactory charge-discharge characteristics.

Although the foregoing techniques suggest that stabilized charge-discharge behavior of high safety is available, the aliphatic salts melting at room temperature and exemplified are all compounds having high viscosity, failing to afford electrolytic solutions which are fully satisfactory in electric conductivity even if the salts are used as admixed with an organic solvent of low viscosity. The use of the salts gives cells increased internal resistance especially over a low temperature range. If a large amount of organic solvent is added to reduce viscosity, then electrolytic solution has high inflammability, lowering flame-retardant effect by containing room temperature molten salt.

[DISCLOSURE OF THE INVENTION]

[PROBLEM TO BE SOLVED BY THE INVENTION]

The present invention relates to nonaqueous electrolytic lithium secondary batteries, an object of the present invention is to solve the above problem, and provides a nonaqueous electrolytic lithium secondary cell which is excellent in safety, has improved electric conductivity at a low temperature range, and stabilized charge-discharge characteristics.

10 [MEANS FOR SOLVING THE PROBLEM]

We have conducted intensive research, have succeeded to solve the above problem, and provide a nonaqueous electrolytic lithium secondary cells which contain a room temperature molten salt, i.e., a combination of an aliphatic quaternary ammonium salt of the formula (1) and a fluorine-containing anion, a specific organic solvent, a specific lithium salt, positive electrode, negative electrode and separator.

In the nonaqueous electrolytic lithium secondary cell having the above components, the cell has enhanced safety due to flame-retardant effect by containing room temperature molten salt.

In the present nonaqueous electrolytic lithium secondary cell, room temperature molten salt of the formula (1) per se, which is not disclosed or suggested in the prior art Patent Literatures 2 to 4, has high electric conductivity and is suitably used in a nonaqueous electrolytic lithium secondary cell.

(formula 1) $N R^1 R^2 R^3 R^4 X^1$

(wherein at least one of R^1 to R^4 are each a hydrocarbon group having 1 to 4 carbon atoms and containing an ether group, two of R^1 , R^2 , R^3 and R^4 may bond together to form a ring, and X^1 is a fluorine-containing anion.)

Further, among salts melting at room temperature of the formula (1), the salt of the formula (3) is particularly excellent in electric conductivity and is particularly suited for use in a nonaqueous electrolytic lithium secondary cell.

In the present nonaqueous electrolytic lithium secondary cell, the cell is characterized in containing a specific organic solvent. The specific organic solvent is contributable to reduce a viscosity of electrolytic solution and enhance electric conductivity at a low temperature range. Further by using a specific organic solvent, a film known as SEI (Solid Electrolyte Interface) is formed on the surface of the negative electrode for selectively passing lithium ions therethrough. The film suppresses the decomposition of the room temperature molten salt, inhibiting ammonium cations from becoming inserted into the negative electrode material. Particularly preferable case is that the organic solvent contains vinylene carbonate, thereby affording stabilized charge-discharge characteristics.

Although the lithium salt is not particularly limited, it is desired that one of the fluorine-containing anions X^1 and X^2 forming the respective room temperature molten salt and the lithium salt contain tetrafluoroborate, thereby affording excellent charge-discharge characteristics. Although the

reason still remains to be clarified, the desirable result appears attributable to the presence of tetrafluoroborate which forms a passive film on the surface of an aluminum member serving as a positive electrode current collector, inhibiting the aluminum from dissolving out.

The present nonaqueous electrolytic lithium secondary cell having the above components is excellent in safety, has improved electric conductivity at a low temperature range, and stabilized charge-discharge characteristics.

10 [EFFECT OF THE INVENTION]

The present nonaqueous electrolytic lithium secondary cell is excellent in safety by containing a room temperature molten salt, has improved electric conductivity at a low temperature range and stabilized charge-discharge characteristics by using a mixture of a specific room temperature molten salt and an organic solvent.

[BEST MODE FOR CARRYING OUT THE INVENTION]

The present invention will be described below in detail.

20 The present invention provides nonaqueous electrolytic lithium secondary cells which contain a room temperature molten salt, i.e., a combination of an aliphatic quaternary ammonium salt of the formula (1) and a fluorine-containing anion, a specific organic solvent, a specific lithium salt, positive electrode, negative electrode and separator.

Aliphatic quaternary ammonium cations for forming the room temperature molten salt and useful for the invention are not limited, and examples thereof are

trimethylmethoxymethylammonium, dimethyl-
 ethylmethoxymethylammonium, dimethylpropylmethoxymethyl-
 ammonium, dimethylbutylmethoxymethyl ammonium,
 diethylmethoxymethyl ammonium, methylethylpropyl-
 5 methoxymethyl ammonium, triethylmethoxymethyl ammonium,
 diethylpropylmethoxymethyl ammonium, diethylbutylmethoxy-
 methyl ammonium, dipropylmethoxymethyl ammonium,
 dipropylethylmethoxymethyl ammonium, tripropylmethoxymethyl
 ammonium, tributylmethoxymethyl ammonium, trimethylethoxy-
 10 methyl ammonium, dimethylethylethoxymethyl ammonium,
 dimethylpropylethoxymethyl ammonium, dimethylbutylethoxy-
 methyl ammonium, diethylmethylethoxymethyl ammonium,
 triethylethoxymethyl ammonium, diethylpropylethoxymethyl
 ammonium, diethylbutylethoxymethyl ammonium, dipropylmethyl-
 15 ethoxymethyl ammonium, dipropylethylethoxymethyl ammonium,
 tripropylethoxymethyl ammonium, tributylethoxymethyl
 ammonium, methylmethoxymethyl pyrrolidinium,
 ethylmethoxymethyl pyrrolidinium, propylmethoxymethyl
 pyrrolidinium, butylmethoxymethyl pyrrolidinium,
 20 methylethoxymethyl pyrrolidinium, ethylethoxymethyl
 pyrrolidinium, propylethoxymethyl pyrrolidinium,
 butylethoxymethyl pyrrolidinium, methylpropoxymethyl
 pyrrolidinium, ethylpropoxymethyl pyrrolidinium,
 propylpropoxymethyl pyrrolidinium, butylpropoxymethyl
 25 pyrrolidinium, methylmethoxymethyl piperidinium,
 ethylmethoxymethyl piperidinium, propylmethoxymethyl
 piperidinium, butylmethoxymethyl piperidinium,
 methylethoxymethyl piperidinium, methylpropoxymethyl

piperidinium, ethylpropoxymethyl piperidinium, propylpropoxymethyl piperidinium, butylpropoxymethyl piperidinium, etc.

Preferable are trimethylmethoxymethyl ammonium,
 5 dimethylethylmethoxymethyl ammonium, dimethylpropylmethoxymethyl ammonium, methylethylpropylmethoxymethyl ammonium, trimethylethoxymethyl ammonium, dimethylethylethoxymethyl ammonium, dimethylpropylethoxymethyl ammonium, methylethylpropylethoxymethyl ammonium, methylmethoxymethyl
 10 pyrrolidinium, ethylmethoxymethyl pyrrolidinium, methylethoxymethyl pyrrolidinium, ethylethoxymethyl pyrrolidinium, methylmethoxymethyl piperidinium, ethylmethoxymethyl piperidinium, methylethoxymethyl piperidinium, and ethylethoxymethyl piperidinium.

15 More preferable are trimethylmethoxymethyl ammonium, dimethylethylmethoxymethyl ammonium, methylethylpropylmethoxymethyl ammonium, trimethylethoxymethyl ammonium, dimethylethylethoxymethyl ammonium, methylmethoxymethyl pyrrolidinium, ethylmethoxymethyl pyrrolidinium and
 20 methylethoxymethyl pyrrolidinium.

Particularly preferable are trimethylmethoxymethyl ammonium, diethylmethylethylmethoxymethyl ammonium and methylmethoxymethyl pyrrolidinium.

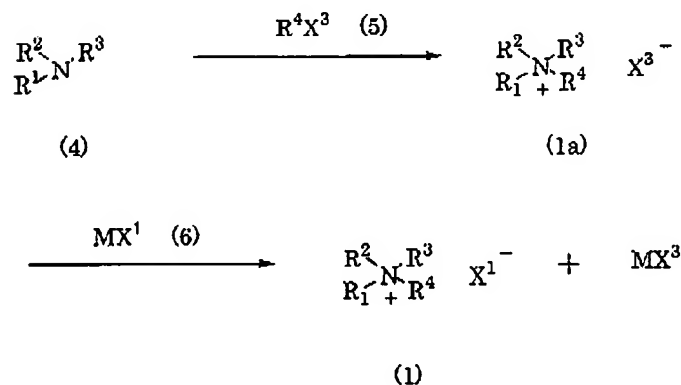
Examples of fluorine-containing anions for forming the
 25 room temperature molten salt and the lithium salt for use in the present invention are BF_4^- , PF_6^- , CF_3SO_3^- , $\text{N}(\text{CF}_3\text{SO}_2)_2^-$, $\text{N}(\text{CF}_3\text{SO}_2)(\text{CF}_3\text{CO})^-$, $\text{N}(\text{CF}_3\text{SO}_2)(\text{C}_2\text{F}_5\text{SO}_2)^-$, etc. Examples of more preferred anions are BF_4^- , PF_6^- and $\text{N}(\text{CF}_3\text{SO}_2)_2^-$. Particularly

preferred are BF_4^- and $\text{N}(\text{CF}_3\text{SO}_2)_2^-$.

The above room temperature molten salt composed by an ammonium cation and a fluorine-containing anion, and lithium salt composed by a lithium ion and a fluorine-containing anion, are each usable singly or at least two of them, respectively. It is desired that one of the fluorine-containing anions forming the respective room temperature molten salt and the lithium salt contain BF_4^- .

The room temperature molten salt and useful for the invention is prepared by various processes. Typical of such processes is represented by the following formula.

(Process for preparing the room temperature molten salt)



15

An aliphatic quaternary ammonium salt of the formula (1a) is prepared by reacting an aliphatic tertiary ammonium of the formula (4) with a compound of the formula (5) wherein X^3 is Cl, Br, I or the like.

The quaternary ammonium salt of the formula (1a) is then reacted with a compound of the formula (6), whereby the aliphatic quaternary ammonium salt of the formula (1) wherein

20

X^1 is other than X^3 is prepared (provided that at least one of R^1 , R^2 , R^3 and R^4 is represented by the formula 4).

The atoms represented by M in the formula (6) include H, alkali metal atoms such as Na, K and Li, alkaline earth metal atoms such as Ca, Mg and Ba and metal atoms such as Ag. X^1 is, for example, BF_4 , PF_6 , CF_3SO_3 , $N(CF_3SO_2)$, $N(CF_3SO_2)(CF_3CO)$ or $N(CF_3SO_2)(C_2F_5SO_2)$.

The aliphatic tertiary ammonium of the formula (4) and the compound of the formula (5) are each a known compound.

Examples of aliphatic tertiary ammonium of the formula (4) are trimethyl ammonium, ethyldimethyl ammonium, dimethylpropyl ammonium, butyldimethyl ammonium, ethylmethylpropyl ammonium, butylethylmethyl ammonium, butylmethylpropyl ammonium, butylethylpropyl ammonium, diethylmethyl ammonium, methyldipropyl ammonium, dibutylmethyl ammonium, triethyl ammonium, ethyldipropyl ammonium, ethyldibutyl ammonium, tripropyl ammonium, methyl pyrrolidinium, ethyl pyrrolidinium, propyl pyrrolidinium, butyl pyrrolidinium ammonium, methyl piperidinium, ethyl piperidinium, propyl piperidinium, butyl piperidinium, dimethylmethoxymethyl ammonium, dimethylethoxymethyl ammonium, dimethylpropoxymethyl ammonium, ethylmethylmethoxymethyl ammonium, ethylmethylethoxymethyl ammonium, ethylmethylpropoxymethyl ammonium, methylpropylmethoxymethyl ammonium, methylpropylethoxymethyl ammonium, methylpropylpropoxymethyl ammonium, butylmethylmethoxymethyl ammonium, diethylmethoxymethyl ammonium, diethylethoxymethyl ammonium, diethylpropoxymethyl

ammonium, ethylpropylmethoxymethyl ammonium,
 ethylpropylethoxymethyl ammonium, ethylpropylpropoxymethyl
 ammonium, butylethylmethoxymethyl ammonium,
 butylethylethoxymethyl ammonium, butylethylpropoxymethyl
 5 ammonium, dipropylmethoxymethyl ammonium,
 dipropylethoxymethyl ammonium, dipropylpropoxymethyl
 ammonium, butylpropylmethoxymethyl ammonium,
 butylpropylethoxymethyl ammonium, butylpropylpropoxymethyl
 ammonium, dibutylmethoxymethyl ammonium, dibutylethoxymethyl
 10 ammonium, dibutylpropoxymethyl ammonium, methoxymethyl
 pyrrolidinium, ethoxymethyl pyrrolidinium, propoxymethoxy
 pyrrolidinium, methoxymethyl piperidinium, ethoxymethyl
 piperidinium, propoxymethyl piperidinium, etc. Useful
 ammoniums are not limited to these amines. Examples of the
 15 compounds of the formula (5) are chloromethyl methyl ether,
 bromomethyl methyl ether, iodomethyl methyl ether, methyl
 iodide, ethyl iodide, ethyl bromide, n-propyl chloride, n-
 propyl bromide, n-propyl iodide, iso-propyl chloride, iso-
 propyl bromide, iso-propyl iodide, n-butyl chloride, n-butyl
 20 bromide, n-butyl iodide, iso-butyl chloride, iso-butyl
 bromide, iso-butyl iodide, tert-butyl chloride, tert-butyl
 bromide, tert-butyl iodide, etc. The two compounds are
 reacted in a suitable solvent.

The solvent to be used can be a wide variety of known
 25 solvents insofar as they are capable of solving the aliphatic
 tertiary ammonium of the formula (4) and the compound of the
 formula (5) and will not adversely affect the reaction.
 Examples of such solvents are benzene, toluene, xylene and

like aromatic hydrocarbons, dichloromethane, chloroform, carbon tetrachloride and like hydrocarbon halides, methanol, ethanol, isopropanol, n-butanol, tert-butanol and like lower alcohols, acetone, methyl ethyl ketone and like ketones, 5 diethyl ether, diisopropyl ether and like ethers, n-hexane, n-heptane and like aliphatic hydrocarbons, cyclohexane and like aliphatic hydrocarbons, etc. Preferable among these solvents are toluene and like aromatic hydrocarbons and chloroform and like hydrocarbon halides. These solvents can 10 be used singly, or at least two of them are usable in admixture.

The aliphatic tertiary ammonium of the formula (4) and the compound of the formula (5) are used in the ratio usually of 0.5 to 5 moles, preferably 0.9 to 1.2 moles, of the latter 15 per mole of the former.

The reaction of the aliphatic tertiary ammonium of the formula (4) with the compound of the formula (5) is conducted usually at -10 to 25° C. The reaction is completed generally in several hours to about 72 hours.

20 The reaction of the quaternary ammonium salt of the formula (1a) obtained above with the compound of the formula (6) is conducted usually by a salt exchange reaction.

The compound of the formula (6) used as a starting material is a known compound. Examples of these are HBF_4 , 25 LiBF_4 , NaBF_4 , KBF_4 , AgBF_4 , HPF_6 , LiPF_6 , NaPF_6 , KPF_6 , $\text{CF}_3\text{SO}_3\text{H}$, $\text{CF}_3\text{SO}_3\text{Li}$, $\text{CF}_3\text{SO}_3\text{Na}$, $\text{CF}_3\text{SO}_3\text{K}$, $\text{HN}(\text{CF}_3\text{SO}_2)_2$, $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, $\text{NaN}(\text{CF}_3\text{SO}_2)_2$, $\text{K}(\text{CF}_3\text{SO}_2)_2$, $\text{HN}(\text{CF}_3\text{SO}_2)(\text{CF}_3\text{CO})$, $\text{LiN}(\text{CF}_3\text{SO}_2)(\text{CF}_3\text{CO})$, $\text{NaN}(\text{CF}_3\text{SO}_2)(\text{CF}_3\text{CO})$, $\text{KN}(\text{CF}_3\text{SO}_2)(\text{CF}_3\text{CO})$, $\text{HN}(\text{CF}_3\text{SO}_2)(\text{C}_2\text{F}_5\text{SO}_2)$,

$\text{LiN}(\text{CF}_3\text{SO}_2)(\text{C}_2\text{F}_5\text{SO}_2)$, $\text{NaN}(\text{CF}_3\text{SO}_2)(\text{C}_2\text{F}_5\text{SO}_2)$, $\text{KN}(\text{CF}_3\text{SO}_2)(\text{C}_2\text{F}_5\text{SO}_2)$,
etc.

This reaction is conducted in a suitable solvent. The solvent to be used can be a wide variety of known solvents
5 insofar as they are capable of dissolving the quaternary ammonium salt of the formula (1a) and the compound of the formula (6) and will not adversely affect the reaction. Examples of such solvents are water, dichloromethane, chloroform, carbon tetrachloride and like hydrocarbon halides,
10 methanol, ethanol, isopropanol, n-butanol, tert-butanol and like lower alcohols, acetone, methyl ethyl ketone and like ketones, ethyl acetate, butyl acetate and like esters, dimethyl sulfoxide, dimethylformamide and like aprotic polar solvents. Preferable among these are methanol and like lower
15 alcohols, chloroform and like hydrocarbon halides and water. These solvents are usable singly, or at least two of them are usable in admixture.

The quaternary ammonium salt of the formula (1a) and the compound of the formula (6) are used in the ratio usually
20 of 0.5 to 5 moles, preferably 0.9 to 1.2 moles, of the latter per mole of the former.

The reaction of the quaternary ammonium salt of the formula (1a) with the compound of the formula (6) proceeds usually rapidly, so that a solution of the two reactants as
25 dissolved in a solvent is reacted at room temperature for about 10 minutes to about 2 hours.

The desired products obtained by the foregoing respective reactions can each be readily isolated from the

reaction mixture and purified by usual isolating and purifying means such as centrifuging, concentration, washing, organic solvent extraction, chromatography and recrystallization.

5 Stated specifically, the quaternary ammonium salt of the formula (1) wherein X^1 is BF_4 is prepared from a quaternary ammonium salt of the formula (1a) by the reaction procedure to be described below. The quaternary ammonium salt of the formula (1a) is dissolved in one of the lower alcohols
10 mentioned above, and a specified amount of a fluoroborate, such as borofluoric acid or silver borofluoride is added to the solution to conduct a reaction at room temperature for about 30 minutes. The hydrogen halide resulting from the reaction is distilled off, silver halide or like halogen salt
15 is filtered off, and the filtrate is concentrated in a vacuum and dried, whereby the desired compound can be isolated. The hydrogen halide can be removed by a known method, for example, by bubbling of N_2 gas or by distillation in a vacuum.

 The quaternary ammonium salt of the formula (1) wherein
20 X^1 is $N(CF_3SO_2)_2$ is prepared from a quaternary ammonium salt of the formula (1a) by the reaction procedure to be described below specifically. The quaternary ammonium salt of the formula (1a) is dissolved in water, a specified amount of alkali metal salt of bistrifluoromethanesulfonylimide
25 (lithium salt, sodium salt, potassium salt or like salt of bistrifluoromethanesulfonylimide) is added to the solution, followed by a reaction at 0 to 25° C for 30 minutes. The desired product formed is extracted from a suitable solvent

(such as dichloromethane, chloroform or ethyl acetate), and the extract is washed with water, then concentrated in a vacuum and dried, whereby the desired product can be isolated.

5 The organic solvent to be used in nonaqueous electrolytic lithium secondary cells is not limited particularly insofar as the solvent will not produce any adverse effect on the characteristics of cells. Examples of such solvents are cyclic carbonic acid esters, chain carbonic
10 acid esters, phosphoric acid esters, cyclic ethers, chain ethers, lactone compounds, chain esters, nitrile compounds, amide compounds, sulfone compounds, etc. Although not limitative, the solvents given below are more specific examples of useful solvents.

15 Examples of cyclic carbonic acid esters are ethylene carbonate, propylene carbonate, butylene carbonate, vinylene carbononate, vinylethylene carbonate, etc. Examples of chain carbonic acid esters are dimethyl carbonate, ethylmethyl carbonate, diethyl carbonate, etc. Examples of phosphoric
20 acid esters are trimethyl phosphate, triethyl phosphate, ethyldimethyl phosphate, diethylmethyl phosphate, etc. Examples of cyclic ethers are tetrahydrofuran, 2-methyltetrahydrofuran, etc. Examples of chain ethers are dimethoxyethane, etc. Examples of lactone compounds are
25 gamma-butyrolactone and the like. Examples of chain esters are methyl propionate, methyl acetate, ethyl acetate, methyl formate, etc. Examples of nitrile compounds are acetonitrile and the like. Examples of amide compounds are

dimethylformamide and the like. Examples of sulfone compounds are sulfolane, etc. These solvents may be used singly, or at least two of them are usable in admixture.

The organic solvent for use in the present invention
5 preferably contains an organic solvent of the formula A, B or C of claim 2. Examples of solvent of the formula A are ethylene carbonate, vinylene carbononate, butylene carbonate, etc. Examples of solvent of the formula B are ethylene trithiocarbonate, vinylene trithiocarbononate, etc.
10 Examples of solvent of the formula C are ethylene sulfite, etc. Useful solvent are not limited to these solvent. These solvents may be used singly, or at least two of them are usable in admixture.

The organic solvent of the invention preferably contains
15 vinylene carbonate. By containing vinylene carbonate, a film known as SEI (Solid Electrolyte Interface) is formed on the surface of the negative electrode for selectively passing lithium ions therethrough. The film suppresses the decomposition of the room temperature molten salt, inhibiting
20 ammonium cations from becoming inserted into the negative electrode material, thereby affording stabilized charge-discharge characteristics.

The present electrolytic solution comprises as stated above room temperature molten salt, lithium salt and organic
25 solvent. The concentration of the lithium salt is usually 0.1 to 2.0 M, preferably 0.15 to 1.5 M, more preferably 0.2 to 1.2 M, most preferably 0.3 to 1.0 M. If the lithium salt concentration is less than 0.1 M, depletion of lithium ions

will occur in the vicinity of the electrode at a high charge-discharge rate to result in lower charge-discharge characteristics. If the lithium ion concentration is over 2.0 M, the electrolytic solution has an increased viscosity and lower electric conductivity. As stated above, it is desired that one of the anions forming the respective room temperature molten salt and the lithium salt contain BF_4^- . It is desirable to adjust the number of ions contained in the BF_4^- to at least 0.5% of the total number of anions in the electrolytic solution. It is more desirable to adjust the number of ions to at least 0.8% of the total number.

Further, weight ratio of the room temperature molten salt to the organic solvent is preferably up to 1, more preferably up to 0.7, and further preferably up to 0.5. If the weight ratio is in excess of 1, the electrolytic solution has a higher viscosity and lower electric conductivity. The organic solvent preferably contains an organic solvent of the formula A, B or C of claim 2. Although all of the solvents may be those of the formula A, B or C, these solvents are in an amount of preferably 1 to 40 wt.%, more preferably 1 to 30 wt.%, particularly preferably 1 to 20 wt.% and most preferably 1 to 10 wt.%. If less than 1 wt.%, the film does not sufficiently form on the surface of the negative electrode, and producing the decomposition of the room temperature molten salt or insertion into the negative electrode material.

In the present positive electrode, examples of positive electrode active substances are composite oxides of lithium

and transition metal or metals, such as LiCoO_2 , LiNiO_2 , $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$, $\text{LiNi}_{1-y-z}\text{Co}_y\text{Mn}_z\text{O}_2$, $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$, LiMnO_2 , LiMn_2O_4 and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, oxides such as TiO_2 and V_2O_5 , sulfides such as TiS_2 and FeS , etc. From the viewpoint of cell capacity and energy density, composite oxides of lithium and transition metal or metals containing ceramolithium are desirable. Such a positive electrode active substance can be molded into a positive electrode along with known auxiliary conductive agent and binder under pressure. Alternatively, the positive electrode can be made by mixing the positive electrode active substance with pyrrolidine or like organic solvent along with known conductive agent and binder to prepare a paste, coating a current collector of aluminum foil with the paste and drying the coating.

Examples of negative electrode are an alloy of metal lithium and other metal, and a material for lithium ions to be inserted therein and to be released therefrom. Examples of alloys of metal lithium and other metals are Li-Al , Li-Sn , Li-Zn , Li-Si , etc. Examples of materials for lithium ions to be inserted therein and to be released therefrom are carbon materials prepared by firing a resin or pitch, a carbon material obtained by adding a boron compound to such a carbon material, natural graphite, etc. These negative electrode materials can be used singly, or at least two of them are usable in admixture.

Such a negative electrode material can be molded into a negative electrode along with known auxiliary conductive agent and binder under pressure. Alternatively, the negative

electrode can be made by mixing the negative electrode active substance with pyrrolidone or like organic solvent along with known conductive agent and binder to prepare a paste, coating a current collector of copper foil with the paste and drying the coating.

[EXAMPLES]

The present invention will be described in greater detail with reference to the following examples. However, the scope of the invention is not limited to these examples.

10 Preparation Example 1

[Preparation of N,N-diethyl-N-methyl-N-methoxymethylammonium chloride]

A 30.0 g quantity of N,N-diethyl-N-methylammonium (reagent, product of Tokyo Kasei Co., Ltd.) was dissolved in 120 g of toluene, followed by nitrogen replacement. Over a period of 1 hour, 31.2 g of chloromethyl methyl ether (reagent, product of Tokyo Kasei Co., Ltd.) was added dropwise to the solution at 5° C. The mixture was stirred at 5° C for 1 hour, heated to a gradually elevated temperature and stirred at room temperature for 10 hours to complete the reaction. The reaction mixture was filtered, and the solids obtained were washed with 150 g of toluene and 150 g of acetone and then dried in a vacuum, giving 53.7 g of the desired product (white solid).

25 Preparation Example 2

[Preparation of N,N-diethyl-N-methyl-N-methoxymethylammonium bistrifluoromethanesulfonylimide]

A 15.0 g quantity of the N,N-diethyl-N-methyl-N-

methoxymethylammonium chloride was dissolved in 85 g of water, and 26.9 g of lithium bistrifluoromethanesulfonylimide (reagent, product of Aldrich Corp.) was added to the solution at room temperature. The mixture was stirred for 30 minutes, and chloroform was added to the mixture for extraction. The organic layer was washed with 50 g of water 15 times, concentrated in a vacuum and dried, affording 33.4 g of the desired product in the form of a colorless transparent liquid.

10 (Preparation of Electrolytic Solutions)

Nonaqueous electrolytic solutions were prepared in Examples 1 and 2 of the invention using a salt or salts melting at room temperature, i.e., N,N-diethyl-N-methyl-N-methoxymethylammonium bistrifluoromethanesulfonylimide (DEMMOMTFSI) and N,N-diethyl-N-methyl-N-methoxymethylammonium tetrafluoroborate (DEMMOMB₄), a lithium salt or salts, i.e., lithium bistrifluoromethanesulfonylimide (LiTFSI) and lithium tetrafluoroborate (LiBF₄), and nonaqueous solvents, i.e., vinylene carbonate (VC), ethylene carbonate (EC) and ethylmethyl carbonate (EMC) in the corresponding proportions listed in Table 1. For comparison, electrolytic solutions were prepared from LiTFSI, EC and EMC (Comparative Examples 1 and 2), and an electrolytic solution was prepared from LiPF₆, EC and EMC (Comparative Example 3).

25 (Evaluation of Electric Conductivity and Cell Characteristics of the Electrolytic Solution)

An electric conductivity meter, manufactured by Radiometer GmbH, was used for measuring the electric

conductivity. The measuring cell used was CDC641T, product of Radiometer GmbH.

Nonaqueous electrolytic lithium secondary cells of the coin type, like the one shown in FIG. 1, were fabricated.

5 With reference to FIG. 1, indicated at 1 is a negative electrode, at 2 a positive electrode, at 3 a porous separator, at 4 a negative electrode can, at 5 a positive electrode can, at 6 a gasket, at 7 a spacer, and at 8 a spring.

10 The lithium secondary cell shown in FIG. 1 was fabricated by the procedure to be described below. Shown below is preparation of Nngative electrode 1.

Natural graphite and polyvinylidene fluoride (PVdF) serving as a binder were mixed together in a weight ratio of
15 9:1, and N-methylpyrrolidone was added to the mixture to obtain a paste. Copper foil, 22 μm in thickness, was uniformly coated with the paste using an electrode coating applicator. The coated copper foil was dried in a vacuum at 120° C for 8 hours and made into negative electrodes 1, 16 mm
20 in diameter, by an electrode blanking press. Shown below is preparation of positive electrode 2.

A powder of LiCoO_2 , acetylene black serving as a conductive auxiliary agent and PVdF serving as a binder were mixed together in a weight ratio of 90:5:5, and N-
25 methylpyrrolidone was added to the mixture to obtain a paste. The paste was dried in a vacuum at 120° C for 8 hours and made into positive electrodes 2, 16 mm in diameter, by an electrode blanking press.

The negative electrode 1 was placed on the bottom wall of a negative electrode can 4, a porous separator 3 was placed on the electrode, the nonaqueous electrolytic solution prepared in Example 1 was then poured into the can, and a
5 gasket 6 was inserted in place. The positive electrode 2, spacer 7, spring 8 and positive electrode can 5 were thereafter placed in this order over the separator, and the opening portion of the negative electrode can 4 was folded inward to seal off the resulting assembly using a coin-type
10 cell crimping machine, whereby a nonaqueous electrolytic lithium secondary cell was fabricated.

In Example 2 and Comparative Examples 1 to 3, electrolytic solutions were checked for electric conductivity in the same manner as the electrolytic solution of Example 1,
15 and nonaqueous electrolytic lithium secondary cells were fabricated by the same procedure as in Example 1.

The cells fabricated were evaluated in the following manner. Each of the cells was charged at a constant current of 0.4 mA, and when the voltage reached 4.1 V, the cell was
20 charged at a constant voltage of 4.1 V for 1 hour. The cell was discharged at a constant current of 1.0 mA until the voltage dropped to 3 V. The cell was held at 3 V for 1 hour upon the voltage reaching 3 V. This charge and discharge steps were combined together as one cycle.

Table 1

	salts melting at room temperature (wt%)	lithium salt (mol)	Organic solvent (wt%)	Electric Conductivity (mS cm^{-1})		※1
				25°C	-10°C	
Ex. 1	DEMMONTFSI (12.5) +DEMMOMB ₄ (0.5)	LiTFSI (0.5)	VC (5) + EC (15.6) + EMC (54.4)	10	5	good
Ex. 2	DEMMONTFSI (13)	LiTFSI (0.5) + LiBF ₄ (0.025)	VC (5) + EC (15.6) + EMC (54.4)	9.8	4.9	good
Com. Ex. 1	None	LiTFSI (0.5)	EC (25) + EMC (75)	6.5	3.4	No good
Com. Ex. 2	None	LiTFSI (1.0)	EC (25) + EMC (75)	6.6	3.6	No good
Com. Ex. 3	None	LiPF ₆ (1.0)	EC (25) + EMC (75)	8.0	3.1	good

※1 : cell characteristics

5 BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a sectional view of a lithium secondary cell fabricated in examples of the invention.

EXPLANATION OF NUMBERS IN THE DRAWINGS

1 negative electrode, 2 positive electrode, 3 porous separator, 4 negative electrode can, 5 positive electrode can, 6 gasket, 7 spacer, 8 spring